

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
21 June 2001 (21.06.2001)

PCT

(10) International Publication Number  
**WO 01/44386 A1**

(51) International Patent Classification<sup>7</sup>: C09D 11/10, C08L 33/02, 33/08, 33/10, 73/00, 41/00, 27/12

(21) International Application Number: PCT/US00/33409

(22) International Filing Date: 8 December 2000 (08.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/460,959 14 December 1999 (14.12.1999) US

(71) Applicant: LEXMARK INTERNATIONAL, INC.  
[US/US]; Intellectual Property Law Dept., 740 West New Circle Road, Lexington, KY 40550 (US).

(72) Inventors: BEACH, Bradley, Leonard; 1757 Hawthorne Lane, Lexington, KY 40505 (US). HOLLOWAY, Ann, P.; 1136 Chetford Drive, Lexington, KY 40509 (US). SUTHAR, Ajay, Kanubhai; 1316 Norcross Court, Lexington, KY 40513 (US).

(74) Agent: DASPIK, Jacqueline, M.; Lexmark International, Inc., Intellectual Property Law Department, 740 West New Circle Road, Lexington, KY 40550 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

A1

(54) Title: INK COMPOSITIONS

(57) Abstract: The present invention relates to ink compositions. More particularly, the present invention relates to ink compositions comprising a colorant and a polymeric binder having a below ambient glass transition temperature, an average particle diameter above about 200nm and an acid component ranging from about 1 % to about 10 % by weight of the polymeric binder. Additionally, the present invention has the novel and useful feature of resistance to both wet-rub and dry smear as well as increased highlighter

WO 01/44386 A1

**"INK COMPOSITIONS"****Technical Field**

This invention relates to the field of ink compositions for ink jet printers.

**Background Art**

The present invention relates to ink compositions for ink jet printers. More particularly, the present invention relates to ink compositions comprising a colorant and a polymeric binder.

Ink jet printing is a conventional technique by which printing is normally accomplished without contact between the printing apparatus and the substrate, or medium, on which the desired print characters are deposited. Such printing is accomplished by ejecting ink from the ink jet printhead of the printing apparatus via numerous methods which employ, for example, pressurized nozzles, electrostatic fields, piezo-electric elements and/or heaters for vapor phase bubble formation.

The ink compositions used in ink jet printing typically employ an aqueous carrier, usually water, colorants and low molecular weight water miscible materials. The colorants which may be employed include dyes and pigments. Pigments provide improved properties such as improved print quality, lightfastness and waterfastness. Unlike dyes, which penetrate into the substrate along with the other components of the ink, pigments tend to sit on top of the substrate. As a result of the physical properties of pigments, pigment based ink compositions have a tendency to dry smear, have low resistance to wet-rub and have low highlighter resistance. The term "dry smear," as used herein, means applying abrasive pressure across the printed substrate and measuring any smear created thereby. The term "wet-rub," as used herein, means applying a drop of water to the

printed substrate followed by applying abrasive pressure across the printed substrate using a cloth and measuring the optical density of the residual ink which lifts from the substrate onto the cloth; wet-rub differs from waterfastness because abrasion is used. The term "highlighter resistance," as used herein, means applying abrasive pressure across the 5 printed substrate with a commercially available highlighting marker and measuring any smear created thereby; an example of such marker is Sanford Corp. MAJOR ACCENT brand highlighting markers. To solve this problem, the present invention was developed to provide an ink composition comprising a colorant and a polymeric binder that improves the resistance of the printed ink to dry smear and wet-rub and provides better highlighter 10 resistance when the ink is jetted onto the substrate. The present invention has demonstrated the ability to resist smearing upon dry smear and wet-rub as well as increased highlighter resistance.

Polymers have been added to ink jet ink compositions to improve durability, to improve print quality and to reduce color bleeding and feathering. However, the inclusion 15 of polymers has resulted in increased printhead maintenance problems, including clogging of the nozzles and kogation, i.e. formation of film on or about the heater. Also, polymers may tend to form films on the nozzle plate. The addition of polymers to ink compositions also may cause decreased pigment dispersion stability and interference with bubble formation. Existing inventions have attempted to address the problems, such as kogation, 20 clogging and other malfunctioning of the printhead, that result from the incorporation of polymers into ink compositions

U.S. Patent No. 5,814,685 to Satake, et al. (hereinafter referred to as "Satake") discloses an ink composition in which pigment and a resin are dispersed in an aqueous medium. Satake further teaches that the resin is a polymeric core/shell material with a glass transition temperature (Tg) of the core in the range of from -100°C to 40°C, and a Tg of the shell in the range from 50°C to 150°C, and an average particle size of 20 to 200nm. Satake teaches that particle size greater than 200nm causes increased maintenance problems.

U.S. Patent Application Serial No. 08/987,185 filed 12/08/97 to Kappele, et al. and assigned to Lexmark International, Inc. (hereinafter referred to as "Kappele") discloses wet-rub resistant ink compositions. Kappele teaches an ink composition utilizing specific copolymers and/or terpolymers as binders, which encapsulate or cover the colorants and form a film on the substrate when the ink is jetted.

U.S. Patent No. 5,679,724 to Sacripante, et al. (hereinafter referred to as "Sacripante") discloses an ink for ink jet printing including a pigment and an emulsifiable polymer resin. Further, Sacripante discloses a Tg range of 10°C - 100°C, preferably 35°C - 80°C. Sacripante teaches that if the Tg is too low, the print media becomes sticky.

European Patent Application No. 851 010 of inventor Anton, et al. (hereinafter referred to as "Anton") discloses an ink composition utilizing a core/shell emulsion polymer with a pigment as the colorant. Further, Anton teaches adding core/shell emulsion polymers to inks containing insoluble colorants in effective quantities to improve waterfastness. Anton illustrates a core/shell emulsion polymer containing two

distinct phases having different T<sub>g</sub>, i.e. one phase has a T<sub>g</sub> above ambient temperature and the other phase has a T<sub>g</sub> below ambient temperature.

European Patent Application No. 704 303 of inventors Fujisawa, et al. (hereinafter referred to as "Fujisawa") discloses an ink composition comprising a colorant, a 5 thermoplastic resin and water. Fujisawa teaches that the thermoplastic resin has a T<sub>g</sub> of 50° - 150°C. Fujisawa further teaches that the particle diameter of the thermoplastic resin is less than 300nm, preferably 50-200nm.

European Patent Application No. 887 391 of inventors Kubota, et al. (hereinafter referred to as "Kubota") discloses an ink composition which comprises a colorant, an 10 inorganic oxide colloid, an alkali metal hydroxide and an aqueous solvent. Kubota teaches including a resin emulsion having a particle size less than 150nm, preferably 5 – 100nm.

European Patent Application No. 869 160 A2 of inventors Nichols, et al. (hereinafter referred to as "Nichols") discloses an inkjet ink formulation with colorant, 15 vehicle and resin emulsion containing ionic carboxylic groups on the surface of resin emulsion particles to cause disassociation of the colorant and resin particles. The resin of Nichols has 1 to 40 wt.% "carboxylic acid groups", and T<sub>g</sub> of 0°C to 120°C; exemplified embodiments of the resin include copolymers of butyl acrylate, methyl methacrylate and (meth)acrylic acid, with 3 to 20 wt.% acid, T<sub>g</sub> of 53°C to 95°C and particle size of 63 nm 20 to 235 nm, utilizing high T<sub>gs</sub> and low particle sizes. Nichols asserts that the inks have good water resistance, however the tests of Nichols only assessed passive water bleed, and did not assess the commercially critical wet-rub resistance or highlighter resistance.

As illustrated by Satake, Fujisawa and Kubota, prior research in this area teaches that smaller binder particles, generally less than about 200nm average diameter, are preferred, presumably as a result of anticipating lowered maintenance problems such as clogging of the ink jet printhead nozzles. As illustrated by Sacripante and Fujisawa, prior 5 research teaches that the apparent Tg of the binder should be significantly above ambient temperature (i.e., above about 25°C) to avoid maintenance problems such as kogation.

As illustrated by Kappele and Anton, prior research teaches that resistance to wet-rub may be incorporated into inks by utilizing polymer resins or core/shell polymer emulsions.

10 As identified above, the challenge and problem presented by the prior art are to develop an inkjet ink binder which will remain dispersed in the complete inkjet ink formulation, will not clog the printhead nozzle or other aspects of the print mechanism, will form a film or other means to bind the pigment together and onto the surface of the paper or other print medium, and will provide a printed ink which is wet-rub, dry smear, 15 scrub and highlighter resistant. The present invention solves all of these problems by use of a polymeric binder as described herein.

Contrary to accepted research and knowledge, the present invention provides for an ink composition comprising a colorant and a polymeric binder wherein the polymeric binder has an average particle diameter of greater than about 200nm, a below ambient Tg 20 of about -10°C and an acid component content of about 1% to about 10% by weight of the binder. Unlike the prior inventions, the present invention provides improved resistance to

dry smear, improved resistance to wet-rub, and improved highlighter resistance without creating the printhead maintenance problems of kogation and clogging.

### Summary of the Invention

The present invention is an aqueous ink. More specifically, this invention relates

- 5 to inks comprising a colorant and a polymeric binder wherein the binder has suitable glass transition temperature ("Tg"), particle size, and charge such that there is no adverse interaction between the ink, the polymeric binder, and the printhead, and such that the resultant ink demonstrates acceptable maintenance, improved resistance to dry smear, improved resistance to wet-rub and highlighter resistance. The ink composition of the
- 10 present invention includes a colorant and a polymeric binder with the extraordinary and unexpected properties of providing an ink jet ink composition which successfully adheres to the substrate without experiencing wet-rub or dry smear, with increased highlighter resistance and without causing increased printhead maintenance problems due to clogging, kogating and other malfunctioning of the nozzles.

- 15 An ink composition utilizing a polymeric binder with a below ambient Tg is an object of this invention. A polymeric binder with a below ambient Tg removes the requirement that the ink composition be heated to activate the polymer binder after jetting. Typically, a polymeric binder with a below ambient Tg generally causes increased maintenance problems such as kogation and clogging, and further, generally such inks
- 20 including such a polymeric binder do not jet.

These and other objectives of the present invention will become apparent from a description of the preferred embodiments herein, and from the claims, which will further define the scope of this invention.

#### Description of the Preferred Embodiments

5       The ink composition according to the present invention contains a colorant, a polymeric binder, and an aqueous carrier. Each of these required components, as well as some optional components, is described in detail below.

The colorant of the present invention may be a dye or a pigment, and preferably is a pigment. Preferably the colorant is a water insoluble pigment. The colorant may be a  
10 self-dispersed pigment, a pigment mixed with a dispersant, or a combination of these. There is essentially no limitation with respect to the colorants which may be utilized in preparing the ink compositions of the present invention. In one embodiment, the colorant is present at from about 0.5% to about 7% by weight of the final ink composition, in another embodiment, the colorant is present at from about 1% to about 5% by weight of  
15 the final ink composition, and in yet another embodiment, the colorant is present at from about 2% to about 4% by weight of the final ink composition.

There is no limitation with respect to the pigments that may be employed in this invention other than that they are capable of resulting in an ink. Any of the commonly employed organic or inorganic pigments may be used. An illustrative example of the  
20 pigments which may be employed in this invention includes azo pigments such as condensed and chelate azo pigments; polycyclic pigments such as phthalocyanines, anthraquinones, quinacridones, thioindigoids, isoindolinones, quinophthalones. Still other pigments which

may be employed include, for example, nitro pigments, daylight fluorescent pigments, carbonates, chromates, titanium oxides, zinc oxides, iron oxides and carbon black. Such pigments may be prepared via conventional techniques and many are commercially available.

The pigment particle size ranges from about 10nm to about 250nm, and in one embodiment, it is about 130nm. There are many art recognized techniques to prepare pigment for inks including preparation of self-dispersed pigment and preparation of pigment-dispersant mixtures. A process for preparing pigment dispersions used in inks is disclosed in U.S. Patent No. 5,891,231 to Gnerlich, et al. and assigned to Lexmark International, Inc., which disclosure is incorporated by reference herein. Examples of 10 pigments which may be used in the present invention are carbon black, such as Monarch 700, Monarch 880, Monarch 800, Regal 250R, Mogul L (from Cabot Corporation), FW18, FW200, Special Black 4A, Printer 95 (from Degussa Corporation), Raven 3500, Raven 1170 and Raven 2500 (from Columbian Chemicals Company); yellow pigment, such as pigment yellow 74 and pigment yellow 13 (from Sun Chemical Corporation), 15 pigment yellow 138 (from Toyo Manufacturing); cyan pigment, such as pigment blue 15:3 (from Sun Chemical Corporation) and pigment blue 15:3 (from Toyo Manufacturing); and magenta pigment, such as pigment red 122, pigment red 57 and pigment red 81 (from Sun Chemical Corporation), pigment red 122 (from Toyo Manufacturing). Such examples are not meant to be limiting, and, as is art recognized, 20 other sources and grades of carbon black, yellow pigment, cyan pigment and magenta pigment may be utilized in the present invention.

The polymeric binder of the present invention comprises a polymer or copolymer formed from monomer classes, including, but not limited to: acrylate esters, methacrylate esters, styrenes, substituted styrenes, vinyl acrylates, vinyl acetates, fluoromethacrylates, acrylamides, substituted acrylamides, methacrylamides, substituted methacrylamides, and combinations thereof. Among the esters of acrylic acid and methacrylic acid, preferred monomers include methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, lauryl methacrylate, and isobutylene methacrylate. Reference is made to contemporaneously filed U.S. Provisional Patent Application Serial No. \_\_\_\_\_, 5 titled "Polymeric Binder for Water-Resistant Ink Jet Inks," by Freeman, et al., assigned to Rohm and Haas Company, which application is incorporated by reference herein. In one embodiment, the binder comprises copolymer of butyl acrylate and methyl methacrylate. In a more specific embodiment, the polymeric binder comprises a co-polymer ranging from about 20% to about 40% by weight of methyl methacrylate and about 60% to about 10 15 20 10% by weight of butyl acrylate. The polymeric binder may comprise a copolymer ranging from about 27% to about 33% by weight of methyl methacrylate and about 66% to 72% by weight of butyl acrylate. In another embodiment, the polymeric binder comprises 10% to 50% by weight methyl methacrylate, 50% to 85% by weight butyl acrylate, and 3% to 10% by weight methacrylic acid, based on the total weight of the polymeric binder; for example 14.5% by weight methyl methacrylate, 80.5% by weight butyl acrylate, and 5% by weight methacrylic acid. The foregoing merely represent example of suitable polymeric binder compositions. The polymeric binders of the

invention comprise polymer or copolymers with from 1 to 10% by weight acid component, based on the total weight of the polymeric binder. In the examples of ink compositions below, the polymeric binder is present at about 0.5% and at about 3% by weight of the ink composition. It should be noted, however, that the present invention

5 includes ink compositions where the polymeric binder may be present at from about 0.1% to about 10% by weight of the ink composition.

The polymeric binder further comprises an acid component. The acid component may comprise acrylic acid, methacrylic acid, itaconic acid, vinyl sulfonic acid, maleic acids or combinations thereof, or may be derived from salts or anhydrides of such acids,

10 such as methacrylic or maleic anhydride or sodium vinylsulfonate or acrylomidopropane sulfonate. In one embodiment the acid component is methacrylic acid. In another embodiment, the acid component is methacrylic acid in combination with another acid.

The acid component of the polymeric binder ranges from about 1% to about 10% by

weight of the total weight of the polymeric binder. In one embodiment, when the acid

15 component is methacrylic acid, the acid component is about 1.1% to about 1.5% by weight of the total weight of the polymeric binder. In another embodiment, when the acid component is methacrylic acid, the acid component is about 1.3% by weight of the total weight of the polymeric binder. It should be noted, however, that the examples of ink compositions shown below do not represent the only possible formulations encompassed

20 by the present invention, and that the present invention includes ink compositions when the acid component of the polymeric binder ranges from about 1% to about 10% by weight of the total weight of the polymeric binder.

The optimal Tg range of the polymeric binder is from about -20°C to about 70°C.

In one embodiment, the optimal preferable Tg range is from about -12°C to about 25°C.

Contrary to art expectations in below ambient temperatures (*i.e.*, below about 25°C), the polymeric binder of the present invention is suitable for use in conventional (*i.e.*, thermal

5 or piezoelectric) ink jet printers and color ink jet printers, for example the Lexmark 7000,

Lexmark 5700, Lexmark Z51 and Lexmark 2050 printers. The Tg of the polymeric

binder may range from about -10°C to about 25°C, or from about -10°C to about 0°C. In

one embodiment, the polymeric binder has a Tg of about -10°C. At these glass transition

temperatures, the binder is believed to form an adhesive film, continuous or otherwise,

10 between the colorant and the substrate as the aqueous ink medium dissipates by

evaporation, absorption by the substrate or otherwise. When the adhesive polymer is not

continuous so as to constitute a true film, the adhesive effect may be achieved through

“spot welds” in which sufficient polymer is present to adhere one or more colorant

particles to the substrate.

15 The polymer particles comprising the polymeric binder have an average diameter

in the range from about 250nm to about 400nm; preferably about 275nm to 350nm.

Contrary to the general principle that smaller polymer particles, especially particles with

average diameter less than 200nm are less likely to cause printhead maintenance

problems, the polymeric binder of the present invention with an average particle diameter

20 ranging from about 275nm to about 400nm provided better overall printability than

binders with larger or smaller particle sizes.

The particle size distribution of the polymeric binder may be unimodal, bimodal or polymodal, provided that the particle size distribution of the polymeric binder particles is such that essentially all the particles fall in the range from 130 to 450nm in diameter. In one embodiment of the invention, the polymeric binder has a bimodal particle size

5 distribution where, preferably, the small size particles have an average diameter in the range from 175 to 260nm, and the large size particles have an average diameter in the range from 260 to 400nm, and the average particle size is within the range from about 250 to 400nm. In another embodiment of the invention, the polymeric binder has a unimodal particle size distribution with an average diameter in the range from 250 to 400nm. In a

10 preferable embodiment, the polymeric binder has a unimodal particle size distribution with an average diameter in the range from 275 to 350nm, more preferably 275 to 300nm; and a particle size distribution such that essentially all the particles fall in the range from 130 to 450nm. The average particle size and particle size distribution may be determined by the capillary hydrodynamic fractionation (CHDF) technique.

15 The molecular weight of the polymeric binder is not critical. However, it has been found that the polymeric binder preferably has a molecular weight in the range from about 10,000 to about 2,000,000 Daltons (Da); more preferably, 50,000 to 1,000,000 Da. The molecular weight, as used herein, is defined as the weight average molecular weight and may be determined by gel permeation chromatography in tetrahydrofuran as solvent. The

20 polymeric binder of the present invention may further comprise additional components which do not substantially alter the characteristics described above, including without limitation process aids such as surfactants, protective colloids, and other stabilizers

known to those skilled in the art. Suitable surfactants, for example, include sodium lauryl sulfate, sodium dodecylbenzene sulfonate, sodium dioctyl sulfosuccinate, and ammonium perflororalkyl sulfonates, Triton X-100, Triton X-405, and polyoxyethyleneated polyoxypropylene glycols.

5       The polymeric binder may be prepared by a conventional persulfate-initiated thermal process known in the art such as batch, semi-batch, gradual addition or continuous. The monomers are polymerized to preferably greater than 99% conversion and then the reaction is cooled to room temperature (20-25°C) after the addition of the appropriate amount of neutralizing base to control pH. The pH is adjusted to between pH  
10      7-10, more preferably between pH 8-9; with neutralizer such as, for example, ammonia, sodium hydroxide, potassium hydroxide or combinations of these neutralizers.  
Preferably, potassium hydroxide is used as neutralizer. The preparation process used has  
been found to make it well suited to the preparation of the polymeric binders of the  
present invention. It allows for controlled particle size and particle size distribution at the  
15     desired acid level range, and a suitable Tg for the resulting polymeric binder.

The polymeric binder may be illustrated, in certain embodiments, through the following examples:

Example I

A sample of binder of the general composition ethyl acrylate (EA), styrene (STY),  
20     and methacrylic acid (MAA) was prepared as follows. After heating a reaction vessel  
containing 400 ml deionized, buffered water (0.06 mmol buffer/gm of water) and 2.1 g  
sodium lauryl sulfate (SLS) to 88°C, 4% of a mixture of 488 g water, 6 g SLS, 714 g EA,

234 g STY and 12.2 MAA was added with 2.7 g sodium persulfate (NaPS) in 12 g of water. This combination was held at 88°C for 10 minutes. Then, the remaining monomer mix was added over a period of 180 minutes, with a cofeed of 1.0 g sodium persulfate in 50 ml water at a rate such that the addition period was 185 minutes.

5 After the cofeed addition was completed, the vessel was held at 88°C for 30 minutes and then cooled. The product was then filtered through 100 and 325 mesh screens. The filtered product was neutralized by combining 865 g of unneutralized product with 735.2 g deionized water and neutralized to pH 8.5 with 10% potassium hydroxide. The average particle size was 280 nm with a particle size distribution ranging  
10 from 175 nm to 400 nm. The calculated Tg was approximately 13°C.

Example 2

A sample of butyl acrylate (BA), methyl methacrylate (MMA), and MAA polymer was prepared according to the procedure in Example 1 except that the monomer mixture consisted of 28.1 g MAA, 663.1 g MMA, 1468.8 g BA and 10.5 g SLS. In this case, a reaction vessel containing 1130 g deionized, buffered water (0.06 mmol buffer/g water) and 4.0 g SLS was heated to 81°C. Then 115.0 g of the monomer mix with a 20 g water rinse was added to the vessel followed by 5.6 g NaPS dissolved in 25 g of water. This combination was held at 81°C for 10 minutes and then the remaining monomer mixture was added over 180 minutes along with an additional 16.5 g SLS and a co-feed of  
15 2.2 g NaPS in 100 g of water (added over 185 minutes). After the co-feed was completed, the reaction was held at 81°C for 30 minutes. Then the product was cooled, filtered and neutralized with the neutralization accomplished by combining 1760 g of unneutralized  
20

product with 1470 g deionized water and brought to a pH of 8.5 with KOH. The resultant polymer had an average particle sized of 286 nm with a particle size distribution ranging from 174 nm to 408 nm. The calculated Tg was 0°C.

Example 3

5        A sample of butyl acrylate (BA), methyl methacrylate (MMA), and acrylic acid (AA) polymer was prepared according to the procedure in Example 2 except that the monomer mixture consisted of 23.5 g AA, 667.7 g MMA, 1468.8 g BA and 10.5 g SLS. In this case, a reaction vessel containing 1130 g deionized, buffered water and 3.0 g SLS was heated to 81°C. The remaining monomer mix, NaPS, as well as an additional 17.5 g  
10      of SLS were fed to the vessel after the initial addition of the mixture. Following neutralization, the resultant polymer had an average particle size of 348 nm with a particle size distribution ranging from 231 nm to 480 nm. The calculated Tg of this polymer was 0°C.

Example 4

15        A sample of butyl acrylate (BA), methyl methacrylate (MMA), and methacrylic acid (MAA) polymer was prepared according to the procedure in Example 2 with the same monomer mixture which consisted of 28.1 g MAA, 663.1 g MMA, 1468.8 g BA and 10.5 g SLS. In this case, a reaction vessel containing 1130 g deionized, buffered water and 3.0 g SLS was heated to 81°C. The remaining monomer mix NaPS, as well as an  
20      additional 17.5 g of SLS were fed to the vessel after the initial addition of the mixture. Following neutralization, the resultant polymer had an average particle size of 301 nm with a particle size distribution ranging from 184 nm to 430 nm. The calculated Tg of

this polymer was 0°C. In an assessment of printability, a sample ink containing 3.0% by weight of the polymer was used to print 90 pages on a Lexmark desktop printer. On the 90<sup>th</sup> page of this print test which was repeated three time, an average of 22 nozzles in the ink cartridge had misfired.

5    Example 5

A sample of butyl acrylate (BA), methyl methacrylate (MMA), and methacrylic acid (MAA) polymer was prepared according to the procedure in Example 2 with the same monomer mixture which consisted of 28.21 g MAA, 663.1 g, 1468.8 g BA and 10.5 g SLS. In this case, a reaction vessel containing 1130 g deionized, buffered water and 5.0 10 g SLS was heated to 81°C. The remaining monomer mix, NaPS, as well as an additional 15.5 g of SLS were fed to the vessel after the initial addition of the mixture. Following neutralization, the resultant polymer had an average particle size of 254 nm with a particle size distribution ranging from 165 nm to 341 nm. The calculated Tg of this polymer was 0°C.

15    Example 6

A sample of butyl acrylate (BA), methyl methacrylate (MMA), and methacrylic acid (MAA) polymer was prepared according to the procedure in Example 2 with a monomer mixture which consisted of 43.2 g MAA, 648.0 g MMA, 1468.8 g BA and 10.5 g SLS. In this case, a reaction vessel containing 1130 g deionized, buffered water and 5.0 20 g SLS was heated to 81°C. The remaining monomer mix, NaPS, as well as an additional 15.5 g of SLS were fed to the vessel after the initial addition of the mixture. Following neutralization, the resultant polymer had an average particle size of 238 nm with a particle

size distribution ranging from 133 nm to 340 nm. The calculated Tg of this polymer was 0°C.

The aqueous carrier of the present invention is water (preferably deionized water).

The aqueous carrier is present at from about 40% to about 95%, may be present at from

5 about 55% to about 80%, and may be present at from about 70% to about 80% by weight of the ink composition. Selection of a suitable mixture for the ink composition of the present invention depends upon the requirements of the specific ink being formulated, such as the desired surface tension and viscosity, the pigment used, the drying time required for the pigmented ink and the type of paper onto which the ink will be printed.

10 The ink composition of the present invention may also include water miscible materials such as humectants, dispersants, penetrants, chelating agents, buffers, biocides, fungicides, bacteriocides, surfactants, anti-curling agents, anti-bleed agents and surface tension modifiers, all as is known in the art. The addition of such materials is generally dictated by the requirements of the specific ink and is used to modify properties of the ink  
15 such as surface tensions and viscosity.

The amount of humectant used is determined by the desired properties of the ink and may range from about 1% to about 30% by weight of the ink composition. Useful humectants include ethylene glycol, 1,3 propanediol, 1,4 butanediol, 1,4 cyclohexanedimethanol, 1,5 pentanediol, 1,6 hexanediol, 1,8 octanediol, 1,2 propanediol,  
20 1,2 butanediol, 1,3 butanediol, 2,3 butanediol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol with average molecular weight of 200, 300, 400, 600, 900, 1000, 1500 and 2000, dipropylene glycol, polypropylene glycol with average

molecular weight of 425, 725, 1000, and 2000, 2-pyrrolidone, 1-methyl-2-pyrrolidone, 1-methyl-2-piperidone, N-ethylacetamide, N-methylpropionamide, N-acetyl ethanolamine, N-methylacetamide, formamide, 3-amino-1, 2-propanediol, 2,2-thiodiethanol, 3,3-thiodipropanol, tetramethylene sulfone, butadiene sulfone, ethylene carbonate, 5 butyrolacetone, tetrahydrofurfuryl alcohol, glycerol, 1,2,4-butenetriol, trimethylpropane, sorbital, pantothenol, Liponic EG-1. Preferred humectants are polyethylene glycol with average molecular weight of 400 to 1000, 2-pyrrolidone, 2,2 thiodiethanol, 1,5 pentanediol, and 1,2 propanediol.

The amount of penetrant used is determined by the desired properties of the ink 10 and may range from about 0.01% to about 10% by weight of the ink composition. Useful penetrants are 1,2 alkyl diols of from 4 to 10 carbon atoms forming the alkyl such as 1,2-hexanediol and others as more fully disclosed in U.S Patent No. 5,364,461 to Beach, et al. and assigned to Lexmark International, Inc., which disclosure is incorporated by reference herein. Useful penetrants include N-propanol, isopropyl alcohol, 1,2 hexanediol, and 15 hexyl carbitol.

The amount of dispersant used is determined by the properties of the colorant when the colorant is a pigment. Useful dispersants are graft copolymers comprising a hydrophilic polymeric segment, a hydrophobic polymeric segment incorporating a hydrolytically-stable siloxyl substituent, and a stabilizing segment. A preferred dispersant 20 is the terpolymer dispersant disclosed in U.S. Patent Nos 5,714,538 and 5,719,204 to Beach, et al. and assigned to Lexmark International, Inc., which disclosures are

incorporated by reference herein. For the purposes of this invention, the dispersant composition is not critical as long as its use results in a stable and printable ink.

The ink composition of the present invention may be prepared by any method known in the art for making such compositions, for example, by mixing, stirring or 5 agitating the ingredients together using any art recognized technique to form an aqueous ink. The procedure for preparation of the ink composition of the present invention is not critical except to the extent that the ink composition is homogenous.

It is expected that the ink composition of the present invention would include any additives necessary to obtain the desired physical properties required for the end use of 10 the ink composition such additives include chelating agents, buffers, biocides, fungicides, bacteriocides, surfactants, anti-curling agents, anti-bleed agents and surface tension modifiers, all as discussed above. Examples of ink composition include the following formulations:

INK COMPOSITION I:

15        4% colorant (mixture of self-dispersed carbon black pigment and mixture of carbon black pigment and dispersant)  
            0.5% polymeric binder (Tg -10°C, particle size 285nm, 1.3% acid component)  
            15% humectant (7.5% polyethylene glycol 400 and 7.5% 2-pyrrolidone)  
            0.75% terpolymer dispersant  
20        0.75% penetrant (hexyl carbitol)  
            balance deionized water

**INK COMPOSITION 2**

4.8% colorant (mixture of carbon black pigment and dispersant)

3% polymeric binder (Tg -10°C, particle size 285nm, 1.3% acid component)

5 15% humectant (5% polyethylene glycol 1000, 5% 2,2-thiodiethanol and 5% 2-pyrrolidone)

1% penetrant (1,2-hexanediol)

balance deionized water

**10 INK COMPOSITION 3**

2.25% colorant mixture of (Toyo cyan pigment and dispersant)

3% polymeric binder (Tg -10°C, particle size 285nm, 1.3% acid component)

20 20% humectant (10% polyethylene glycol 400 and 10% 2,2-thiodiethanol)

15 1% penetrant (1,2-hexanediol)

balance deionized water

**COMPARATIVE INK COMPOSITION A**

4.8% colorant (mixture of carbon black pigment and dispersant)

20 20% humectant (10% polyethylene glycol 400 and 10% 2,2 thiodiethanol)

2% penetrant (N-propanol)

balance deionized water

**COMPARATIVE INK COMPOSITION B**

2.25% colorant (mixture of Toyo cyan pigment and dispersant)

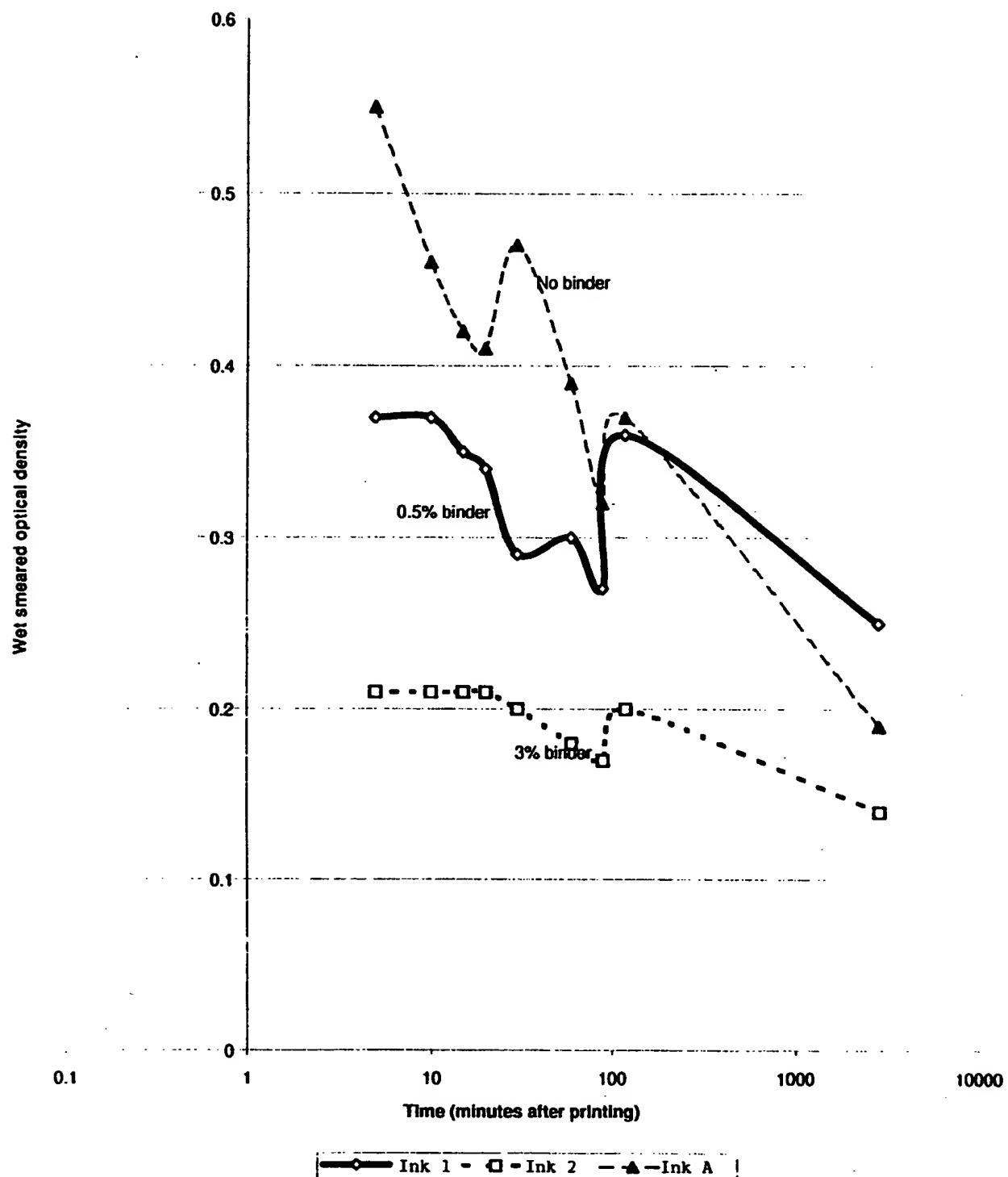
25 20% humectant (10% polyethylene glycol 400 and 10% 2,2-thiodiethanol)

1% penetrant (1,2-hexanediol)

**balance deionized water**

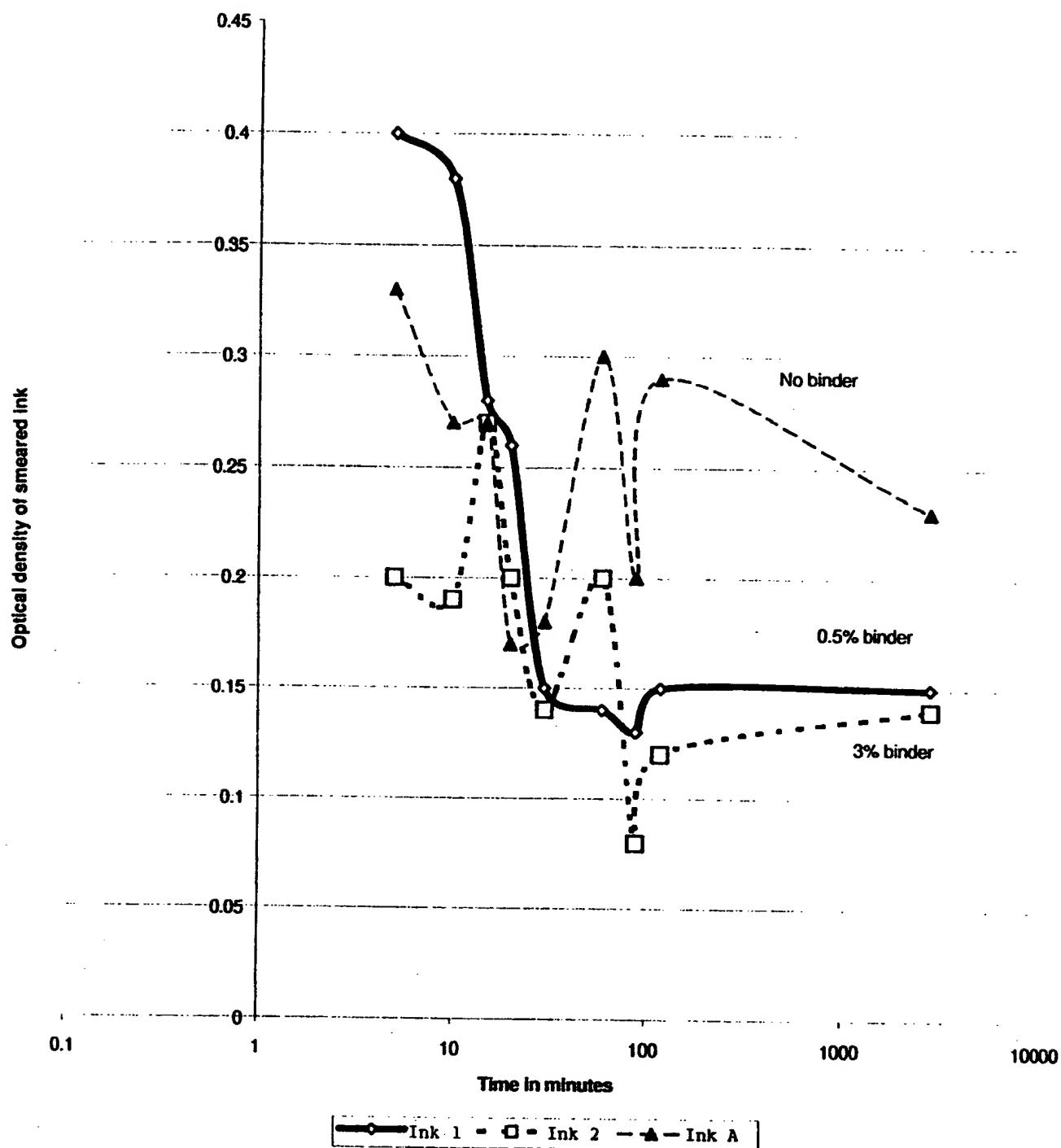
**The resistance of Ink Compositions 1, 2, and A to wet rub was determined by using a commercially available densitometer to measure the optical density of the residual ink on a wet cloth that was rubbed over the printed substrate. The results are shown in Chart 1.**

CHART 1



The resistance of Ink Compositions 1, 2, 3, A and B to highlighter smear was determined by using a commercially available densitometer to measure the optical density of the trailing edge of a highlighter mark after passing over the printed substrate into an unprinted area of the substrate. The results are shown in Chart 2.

CHART 2



Dry smear, water fastness and highlighter resistance were measured to determine how long each ink composition took to reach an acceptable result (ie. no change in optical density after smear/rub). The results are shown in Table 1.

5

Table 1

Test	<u>Ink Composition</u> (time in minutes)				
	1	2	A	3	B
Dry Smear	10	10	10	10	10
Water Fastness	30	10	30	10	10
Highlighter Resistance	180	30	1440	10	60

Although the exact reasons are not known, it is theorized that the polymeric binder particles flow together at a given temperature (generally a temperature above the Tg) binding the pigment particles together to form a film, successfully adhering the pigment particles together and to the substrate. It is believed that the polymeric binder encapsulates the pigment particles in the ink composition. It is further believed that, when jetted, the polymeric binder forms a film on the substrate, holding the pigment particles in place, and adhering the pigment particles to the substrate. The polymeric binder of the present invention with a below ambient Tg forms a good film at room temperature on a wide range of substrates with little or no dry smear, little or no or wet rub and highlighter resistance.

It is also theorized that the larger particle size of the polymeric binder results in fewer particles per milliliter of ink; therefore, there are fewer instances of particles interacting with each other and with the printhead apparatus (eg. nozzle openings, nozzle channels, ink channels, etc.).

**What is claimed is**

- 1. An ink comprising:**
  - a. an aqueous carrier;**
  - b. a colorant; and**
  - c. a polymeric binder having a glass transition temperature ranging from about -20°C to about 25°C, an average particle diameter ranging from about 250nm to about 400nm and an acid component ranging from about 1% to about 10% by weight of said binder.**
- 2. The ink of claim 1 wherein said glass transition temperature of said binder ranges from about -12°C to about 0°C, said average particle diameter of said binder ranges from about 250nm to about 350nm and said acid component of said binder ranges from about 1% to about 3% by weight of said binder.**
- 3. The ink of claim 2 wherein said colorant is one or more of a pigment-dispersant mixture and a self-dispersed pigment.**
- 4. The ink of claim 3 wherein said colorant ranges from about 0.5% to about 7% by weight of said ink and said binder ranges from about 0.1% to about 10% by weight of said ink.**
- 5. The ink of claim 4 wherein said colorant is said self-dispersed pigment and said pigment-dispersant mixture, wherein said colorant ranges from about 1% to about 5% by weight of said ink and said binder is about 0.5% by weight of said ink.**
- 6. The ink of claim 4 wherein said colorant is said pigment-dispersant mixture, wherein said colorant ranges from about 1% to about 5% by weight of said ink and said binder is about 3% by weight of said ink.**

7. The ink of claim 1 wherein said glass transition temperature of said binder ranges from about -12°C to about 0°C, said average particle diameter of said binder ranges from about 250nm to about 350nm and said acid component of said binder is about 1.3%.
8. The ink of claim 7 wherein said colorant is one or more of a pigment-dispersant mixture and a self-dispersed pigment.
9. The ink of claim 8 wherein said colorant ranges from about 0.5% to about 7% by weight of said ink and said binder ranges from about 0.1% to about 10% by weight of said ink.
10. The ink of claim 9 wherein said colorant is said self-dispersed pigment and said pigment-dispersant mixture and wherein said colorant ranges from about 1% to about 5% by weight of said ink and said binder is about 0.5% by weight of said ink.
11. The ink of claim 9 wherein said colorant is said pigment-dispersant mixture and wherein said colorant ranges from about 1% to about 5% by weight of said ink and said binder is about 3% by weight of said ink.
12. The ink of claim 1 wherein said glass transition temperature of said binder ranges from about -12°C to about 0°C, said average particle diameter of said binder ranges from about 250nm to about 350nm and said acid component of said binder ranges from about 4% to about 10% by weight of said binder.
13. The ink of claim 12 wherein said colorant is one or more of a pigment-dispersant mixture and a self-dispersed pigment.

14. The ink of claim 13 wherein said colorant ranges from about 0.5% to about 7% by weight of said ink and said binder ranges from about 0.1 % to about 10 / by weight of said ink.
15. The ink of claim 14 wherein said colorant is said self-dispersed pigment, wherein said colorant ranges from about .1% to about 5% by weight of said ink wherein said binder ranges from about 0.5% to about 3% by weight of said ink.
16. The ink of claim 1 wherein said binder further comprises a mixture of a plurality of larger particles and a plurality of smaller particles wherein said binder mixture having an average particle diameter greater than 200nm and wherein said binder mixture is unimodal.
17. An ink comprising:
  - a. an aqueous carrier;
  - b. a colorant; and
  - c. a polymeric binder consisting essentially of one or more monomers selected from the group consisting of acrylates, methacrylates, substituted styrenes, styrenes, fluoromethacrylates, vinyl acrylates, vinyl acetates, acrylamides, substituted acrylamides, methacrylamides, and substituted methacrylamides and an acid component selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acids, vinylsulfonic acids and acids derived from methacrylic anhydride, maleic anhydride, sodium 5  
10  
15  
20  
25  
30  
35  
40  
45  
50  
55  
60  
65  
70  
75  
80  
85  
90  
95  
100  
105  
110  
115  
120  
125  
130  
135  
140  
145  
150  
155  
160  
165  
170  
175  
180  
185  
190  
195  
200  
205  
210  
215  
220  
225  
230  
235  
240  
245  
250  
255  
260  
265  
270  
275  
280  
285  
290  
295  
300  
305  
310  
315  
320  
325  
330  
335  
340  
345  
350  
355  
360  
365  
370  
375  
380  
385  
390  
395  
400  
405  
410  
415  
420  
425  
430  
435  
440  
445  
450  
455  
460  
465  
470  
475  
480  
485  
490  
495  
500  
505  
510  
515  
520  
525  
530  
535  
540  
545  
550  
555  
560  
565  
570  
575  
580  
585  
590  
595  
600  
605  
610  
615  
620  
625  
630  
635  
640  
645  
650  
655  
660  
665  
670  
675  
680  
685  
690  
695  
700  
705  
710  
715  
720  
725  
730  
735  
740  
745  
750  
755  
760  
765  
770  
775  
780  
785  
790  
795  
800  
805  
810  
815  
820  
825  
830  
835  
840  
845  
850  
855  
860  
865  
870  
875  
880  
885  
890  
895  
900  
905  
910  
915  
920  
925  
930  
935  
940  
945  
950  
955  
960  
965  
970  
975  
980  
985  
990  
995  
1000  
1005  
1010  
1015  
1020  
1025  
1030  
1035  
1040  
1045  
1050  
1055  
1060  
1065  
1070  
1075  
1080  
1085  
1090  
1095  
1100  
1105  
1110  
1115  
1120  
1125  
1130  
1135  
1140  
1145  
1150  
1155  
1160  
1165  
1170  
1175  
1180  
1185  
1190  
1195  
1200  
1205  
1210  
1215  
1220  
1225  
1230  
1235  
1240  
1245  
1250  
1255  
1260  
1265  
1270  
1275  
1280  
1285  
1290  
1295  
1300  
1305  
1310  
1315  
1320  
1325  
1330  
1335  
1340  
1345  
1350  
1355  
1360  
1365  
1370  
1375  
1380  
1385  
1390  
1395  
1400  
1405  
1410  
1415  
1420  
1425  
1430  
1435  
1440  
1445  
1450  
1455  
1460  
1465  
1470  
1475  
1480  
1485  
1490  
1495  
1500  
1505  
1510  
1515  
1520  
1525  
1530  
1535  
1540  
1545  
1550  
1555  
1560  
1565  
1570  
1575  
1580  
1585  
1590  
1595  
1600  
1605  
1610  
1615  
1620  
1625  
1630  
1635  
1640  
1645  
1650  
1655  
1660  
1665  
1670  
1675  
1680  
1685  
1690  
1695  
1700  
1705  
1710  
1715  
1720  
1725  
1730  
1735  
1740  
1745  
1750  
1755  
1760  
1765  
1770  
1775  
1780  
1785  
1790  
1795  
1800  
1805  
1810  
1815  
1820  
1825  
1830  
1835  
1840  
1845  
1850  
1855  
1860  
1865  
1870  
1875  
1880  
1885  
1890  
1895  
1900  
1905  
1910  
1915  
1920  
1925  
1930  
1935  
1940  
1945  
1950  
1955  
1960  
1965  
1970  
1975  
1980  
1985  
1990  
1995  
2000  
2005  
2010  
2015  
2020  
2025  
2030  
2035  
2040  
2045  
2050  
2055  
2060  
2065  
2070  
2075  
2080  
2085  
2090  
2095  
2100  
2105  
2110  
2115  
2120  
2125  
2130  
2135  
2140  
2145  
2150  
2155  
2160  
2165  
2170  
2175  
2180  
2185  
2190  
2195  
2200  
2205  
2210  
2215  
2220  
2225  
2230  
2235  
2240  
2245  
2250  
2255  
2260  
2265  
2270  
2275  
2280  
2285  
2290  
2295  
2300  
2305  
2310  
2315  
2320  
2325  
2330  
2335  
2340  
2345  
2350  
2355  
2360  
2365  
2370  
2375  
2380  
2385  
2390  
2395  
2400  
2405  
2410  
2415  
2420  
2425  
2430  
2435  
2440  
2445  
2450  
2455  
2460  
2465  
2470  
2475  
2480  
2485  
2490  
2495  
2500  
2505  
2510  
2515  
2520  
2525  
2530  
2535  
2540  
2545  
2550  
2555  
2560  
2565  
2570  
2575  
2580  
2585  
2590  
2595  
2600  
2605  
2610  
2615  
2620  
2625  
2630  
2635  
2640  
2645  
2650  
2655  
2660  
2665  
2670  
2675  
2680  
2685  
2690  
2695  
2700  
2705  
2710  
2715  
2720  
2725  
2730  
2735  
2740  
2745  
2750  
2755  
2760  
2765  
2770  
2775  
2780  
2785  
2790  
2795  
2800  
2805  
2810  
2815  
2820  
2825  
2830  
2835  
2840  
2845  
2850  
2855  
2860  
2865  
2870  
2875  
2880  
2885  
2890  
2895  
2900  
2905  
2910  
2915  
2920  
2925  
2930  
2935  
2940  
2945  
2950  
2955  
2960  
2965  
2970  
2975  
2980  
2985  
2990  
2995  
3000  
3005  
3010  
3015  
3020  
3025  
3030  
3035  
3040  
3045  
3050  
3055  
3060  
3065  
3070  
3075  
3080  
3085  
3090  
3095  
3100  
3105  
3110  
3115  
3120  
3125  
3130  
3135  
3140  
3145  
3150  
3155  
3160  
3165  
3170  
3175  
3180  
3185  
3190  
3195  
3200  
3205  
3210  
3215  
3220  
3225  
3230  
3235  
3240  
3245  
3250  
3255  
3260  
3265  
3270  
3275  
3280  
3285  
3290  
3295  
3300  
3305  
3310  
3315  
3320  
3325  
3330  
3335  
3340  
3345  
3350  
3355  
3360  
3365  
3370  
3375  
3380  
3385  
3390  
3395  
3400  
3405  
3410  
3415  
3420  
3425  
3430  
3435  
3440  
3445  
3450  
3455  
3460  
3465  
3470  
3475  
3480  
3485  
3490  
3495  
3500  
3505  
3510  
3515  
3520  
3525  
3530  
3535  
3540  
3545  
3550  
3555  
3560  
3565  
3570  
3575  
3580  
3585  
3590  
3595  
3600  
3605  
3610  
3615  
3620  
3625  
3630  
3635  
3640  
3645  
3650  
3655  
3660  
3665  
3670  
3675  
3680  
3685  
3690  
3695  
3700  
3705  
3710  
3715  
3720  
3725  
3730  
3735  
3740  
3745  
3750  
3755  
3760  
3765  
3770  
3775  
3780  
3785  
3790  
3795  
3800  
3805  
3810  
3815  
3820  
3825  
3830  
3835  
3840  
3845  
3850  
3855  
3860  
3865  
3870  
3875  
3880  
3885  
3890  
3895  
3900  
3905  
3910  
3915  
3920  
3925  
3930  
3935  
3940  
3945  
3950  
3955  
3960  
3965  
3970  
3975  
3980  
3985  
3990  
3995  
4000  
4005  
4010  
4015  
4020  
4025  
4030  
4035  
4040  
4045  
4050  
4055  
4060  
4065  
4070  
4075  
4080  
4085  
4090  
4095  
4100  
4105  
4110  
4115  
4120  
4125  
4130  
4135  
4140  
4145  
4150  
4155  
4160  
4165  
4170  
4175  
4180  
4185  
4190  
4195  
4200  
4205  
4210  
4215  
4220  
4225  
4230  
4235  
4240  
4245  
4250  
4255  
4260  
4265  
4270  
4275  
4280  
4285  
4290  
4295  
4300  
4305  
4310  
4315  
4320  
4325  
4330  
4335  
4340  
4345  
4350  
4355  
4360  
4365  
4370  
4375  
4380  
4385  
4390  
4395  
4400  
4405  
4410  
4415  
4420  
4425  
4430  
4435  
4440  
4445  
4450  
4455  
4460  
4465  
4470  
4475  
4480  
4485  
4490  
4495  
4500  
4505  
4510  
4515  
4520  
4525  
4530  
4535  
4540  
4545  
4550  
4555  
4560  
4565  
4570  
4575  
4580  
4585  
4590  
4595  
4600  
4605  
4610  
4615  
4620  
4625  
4630  
4635  
4640  
4645  
4650  
4655  
4660  
4665  
4670  
4675  
4680  
4685  
4690  
4695  
4700  
4705  
4710  
4715  
4720  
4725  
4730  
4735  
4740  
4745  
4750  
4755  
4760  
4765  
4770  
4775  
4780  
4785  
4790  
4795  
4800  
4805  
4810  
4815  
4820  
4825  
4830  
4835  
4840  
4845  
4850  
4855  
4860  
4865  
4870  
4875  
4880  
4885  
4890  
4895  
4900  
4905  
4910  
4915  
4920  
4925  
4930  
4935  
4940  
4945  
4950  
4955  
4960  
4965  
4970  
4975  
4980  
4985  
4990  
4995  
5000  
5005  
5010  
5015  
5020  
5025  
5030  
5035  
5040  
5045  
5050  
5055  
5060  
5065  
5070  
5075  
5080  
5085  
5090  
5095  
5100  
5105  
5110  
5115  
5120  
5125  
5130  
5135  
5140  
5145  
5150  
5155  
5160  
5165  
5170  
5175  
5180  
5185  
5190  
5195  
5200  
5205  
5210  
5215  
5220  
5225  
5230  
5235  
5240  
5245  
5250  
5255  
5260  
5265  
5270  
5275  
5280  
5285  
5290  
5295  
5300  
5305  
5310  
5315  
5320  
5325  
5330  
5335  
5340  
5345  
5350  
5355  
5360  
5365  
5370  
5375  
5380  
5385  
5390  
5395  
5400  
5405  
5410  
5415  
5420  
5425  
5430  
5435  
5440  
5445  
5450  
5455  
5460  
5465  
5470  
5475  
5480  
5485  
5490  
5495  
5500  
5505  
5510  
5515  
5520  
5525  
5530  
5535  
5540  
5545  
5550  
5555  
5560  
5565  
5570  
5575  
5580  
5585  
5590  
5595  
5600  
5605  
5610  
5615  
5620  
5625  
5630  
5635  
5640  
5645  
5650  
5655  
5660  
5665  
5670  
5675  
5680  
5685  
5690  
5695  
5700  
5705  
5710  
5715  
5720  
5725  
5730  
5735  
5740  
5745  
5750  
5755  
5760  
5765  
5770  
5775  
5780  
5785  
5790  
5795  
5800  
5805  
5810  
5815  
5820  
5825  
5830  
5835  
5840  
5845  
5850  
5855  
5860  
5865  
5870  
5875  
5880  
5885  
5890  
5895  
5900  
5905  
5910  
5915  
5920  
5925  
5930  
5935  
5940  
5945  
5950  
5955  
5960  
5965  
5970  
5975  
5980  
5985  
5990  
5995  
6000  
6005  
6010  
6015  
6020  
6025  
6030  
6035  
6040  
6045  
6050  
6055  
6060  
6065  
6070  
6075  
6080  
6085  
6090  
6095  
6100  
6105  
6110  
6115  
6120  
6125  
6130  
6135  
6140  
6145  
6150  
6155  
6160  
6165  
6170  
6175  
6180  
6185  
6190  
6195  
6200  
6205  
6210  
6215  
6220  
6225  
6230  
6235  
6240  
6245  
6250  
6255  
6260  
6265  
6270  
6275  
6280  
6285  
6290  
6295  
6300  
6305  
6310  
6315  
6320  
6325  
6330  
6335  
6340  
6345  
6350  
6355  
6360  
6365  
6370  
6375  
6380  
6385  
6390  
6395  
6400  
6405  
6410  
6415  
6420  
6425  
6430  
6435  
6440  
6445  
6450  
6455  
6460  
6465  
6470  
6475  
6480  
6485  
6490  
6495  
6500  
6505  
6510  
6515  
6520  
6525  
6530  
6535  
6540  
6545  
6550  
6555  
6560  
6565  
6570  
6575  
6580  
6585  
6590  
6595  
6600  
6605  
6610  
6615  
6620  
6625  
6630  
6635  
6640  
6645  
6650  
6655  
6660  
6665  
6670  
6675  
6680  
6685  
6690  
6695  
6700  
6705  
6710  
6715  
6720  
6725  
6730  
6735  
6740  
6745  
6750  
6755  
6760  
6765  
6770  
6775  
6780  
6785  
6790  
6795  
6800  
6805  
6810  
6815  
6820  
6825  
6830  
6835  
6840  
6845  
6850  
6855  
6860  
6865  
6870  
6875  
6880  
6885  
6890  
6895  
6900  
6905  
6910  
6915  
6920  
6925  
6930  
6935  
6940  
6945  
6950  
6955  
6960  
6965  
6970  
6975  
6980  
6985  
6990  
6995  
7000  
7005  
7010  
7015  
7020  
7025  
7030  
7035  
7040  
7045  
7050  
7055  
7060  
7065  
7070  
7075  
7080  
7085  
7090  
7095  
7100  
7105  
7110  
7115  
7120  
7125  
7130  
7135  
7140  
7145  
7150  
7155  
7160  
7165  
7170  
7175  
7180  
7185  
7190  
7195  
7200  
7205  
7210  
7215  
7220  
7225  
7230  
7235  
7240  
7245  
7250  
7255  
7260  
7265  
7270  
7275  
7280  
7285  
7290  
7295  
7300  
7305  
7310  
7315  
7320  
7325  
7330  
7335  
7340  
7345  
7350  
7355  
7360  
7365  
7370  
7375  
7380  
7385  
7390  
7395  
7400  
7405  
7410  
7415  
7420  
7425  
7430  
7435  
7440  
7445  
7450  
7455  
7460  
7465  
7470  
7475  
7480  
7485  
7490  
7495  
7500  
7505  
7510  
7515  
7520  
7525  
7530  
7535  
7540  
7545  
7550  
7555  
7560  
7565  
7570  
7575  
7580  
7585  
7590  
7595  
7600  
7605  
7610  
7615  
7620  
7625  
7630  
7635  
7640  
7645  
7650  
7655  
7660  
7665  
7670  
7675  
7680  
7685  
7690  
7695  
7700  
7705  
7710  
7715  
7720  
7725  
7730  
7735  
7740  
7745  
7750  
7755  
7760  
7765  
7770  
7775  
7780  
7785  
7790  
7795  
7800  
7805  
7810  
7815  
7820  
7825  
7830  
7835  
7840  
7845  
7850  
7855  
7860  
7865  
7870  
7875  
7880  
7885  
7890  
7895  
7900  
7905  
7910  
7915  
7920  
7925  
7930  
7935  
7940  
7945  
7950  
7955  
7960  
7965  
7970  
7975  
7980  
7985  
7990  
7995  
8000  
8005  
8010  
8015  
8020  
8025  
8030  
8035  
8040  
8045  
8050  
8055  
8060  
8065  
8070  
8075  
8080  
8085  
8090  
8095  
8100  
8105  
8110  
8115  
8120  
8125  
8130  
8135  
8140  
8145  
8150  
8155  
8160  
8165  
8170  
8175  
8180  
8185  
8190  
8195  
8200  
8205  
8210  
8215  
8220  
8225  
8230  
8235  
8240  
8245  
8250  
8255  
8260  
8265  
8270  
8275  
8280  
8285  
8290  
8295  
8300  
8305  
8310  
8315  
8320  
8325  
8330  
8335  
8340  
8345  
8350  
8355  
8360  
8365  
8370  
8375  
8380  
8385  
8390  
8395  
8400  
8405  
8410  
8415  
8420  
8425  
8430  
8435  
8440  
8445  
8450  
8455  
8460  
8465  
8470  
8475  
8480  
8485  
8490  
8495  
8500  
8505  
8510  
8515  
8520  
8525  
8530  
8535  
8540  
8545  
8550  
8555  
8560  
8565  
8570  
8575  
8580  
8585  
8590  
8595  
8600  
8605  
8610  
8615  
8620  
8625  
8630  
8635  
8640  
8645  
8650  
8655  
8660  
8665  
8670  
8675  
8680  
8685  
8690  
8695  
8700  
8705  
8710  
8715  
8720  
8725  
8730  
8735  
8740  
8745  
8750  
8755  
8760  
8765  
8770  
8775  
8780  
8785  
8790  
8795  
8800  
8805  
8810  
8815  
8820  
8825  
8830  
8835  
8840  
8845  
8850  
8855  
8860  
8865  
8870  
8875  
8880  
8885  
8890  
8895  
8900  
8905  
8910  
8915  
8920  
8925  
8930  
8935  
8940  
8945  
8950  
8955  
8960  
8965  
8970  
8975  
8980  
8985  
8990  
8995  
9000  
9005  
9010  
9015  
9020  
9025  
9030  
9035  
9040  
9045  
9050  
9055  
9060  
9065  
9070  
9075  
9080  
9085  
9090  
9095  
9100  
9105  
9110  
9115  
9120  
9125  
9130  
9135  
9140  
9145  
9150  
9155  
9160  
9165  
9170  
9175  
9180  
9185  
9190  
9195  
9200  
9205  
9210  
9215  
9220  
9225  
9230  
9235  
9240  
9245  
9250  
9255  
9260  
9265  
9270  
9275  
9280  
928

about -20°C to about 25°C and an average particle diameter ranging from about 130nm to about 450nm.

18. The ink of claim 17, wherein said monomers are selected from one or more of alkyl acrylates and alkyl methacrylates.
19. The ink of claim 18, wherein said monomers are selected from one or more of methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate and butyl methacrylate.
20. The ink of claim 19, wherein said monomers are a combination of butyl acrylate and methyl methacrylate.
21. The ink of claim 20, wherein said binder comprises from about 66% to about 72% by weight butyl acrylate and 27% to about 33% weight methyl methacrylate.
22. The ink of claim 17, wherein said acid component is selected from one or more of acrylic acid and methacrylic acid.
23. The ink of claim 17, wherein said glass transition temperature of said binder ranges from about -12°C to about 0°C, said average particle diameter ranges from about 250nm to about 350nm and said acid component ranges from about 1.3% to about 2.5% by weight of said binder.
24. The ink of claim 23, wherein said colorant is one or more of a pigment-dispersant mixture and a self-dispersed pigment.
25. The ink of claim 24 wherein said colorant ranges from about 0.5% to about 7% by weight of said ink and said binder ranges from about 0.1% to about 10% by weight of said ink.
26. The ink of claim 25 wherein said colorant is said self-dispersed pigment and said

pigment-dispersant mixture, wherein said colorant ranges from about 1% to about 5% by weight of said ink and said binder is about 0.5% by weight of ink.

27. The ink of claim 25 wherein said colorant is said pigment-dispersant mixture, wherein said colorant ranges from about 1% to about 5% by weight of said ink and wherein said binder is about 3% by weight of said ink.
28. The ink of claim 18 wherein said binder further comprises a mixture of a plurality of larger particles and a plurality of smaller particles wherein said binder mixture having an average particle diameter greater than 200nm and wherein said binder mixture is unimodal.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/33409

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) :C09D 11/10; C08L 33/02, 33/08, 33/10, 73/00, 41/00, 27/12

US CL :523/160; 524/547, 551, 555, 556, 560

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/160, 161; 524/547, 551, 555, 556, 560, 599; 106/31.6

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0867484 A2 (MIYABAYASHI et al.) 30 September 1998 (30/09/98), page 3, lines 32-33 and 58, page 4, lines 22-24 and 55-58, page 5, lines 8-9, 43-44, and 53, page 6, line 50.	1-2, 4-7, 9-12, 14-19, 22-23, 25, 27-28
Y	US 5,851,274 A (LIN) 22 Decemeber 1998 (22/12/98), col.11, lines 55-67, col.13, lines 58-62, and col.14, lines 41-43.	3, 8, 13, 20-21, 24, 26
Y	US 5,713,989 A (WICKRAMANAYAKE et al.) 03 February 1998 (03/02/98), col.4, lines 52-56 and col.5, lines 5-8.	3, 8, 13, 20-21, 24, 26

 Further documents are listed in the continuation of Box C.

See patent family annex.

• Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

12 JANUARY 2001

Date of mailing of the international search report

15FEB2001

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington DC 20231

Authorized officer

CALLIE SHOSHO

DEBORAH THOMAS,  
PARALEGAL SPECIALIST

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/33409

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,696,182 A (KASHIWAZAKI et al.) 09 December 1997 (09/12/97), col.4, lines 10-13 and 47-48, col.4, line 64-col.5, line 1, col.5, lines 10-20 and 30-33, col.10, line 65-col.11, line 1, col.16, lines 48-51.	17-23, 25, 27
Y, P	US 6,019,828 A (REHMAN) 01 February 2000 (01/02/00), col.2, lines 53-54 and 65, col.3, lines 51-53, col.4, line 53-col.5, line 12, col.5, lines 32-36, col.6, lines 6-16, col.8, lines 26-29.	1-28
A	US 5,877,235 A (SAKUMA et al.) 02 March 1999 (02/03/99)	1-28
A, P	US 6,025,412 A (SACRIPANTE et al.) 15 February 2000 (15/02/00)	1-28
A	JP 10279870 A (NICHOLS et al.) 20 October 1998 (20/10/98)	1-28

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US00/33409

**B. FIELDS SEARCHED**

Electronic data bases consulted (Name of data base and where practicable terms used):

**EAST**

search terms: glass transition, particle size, particle diameter, ink, binder, acrylate, methacrylate, acrylic, methacrylic, ink jet, pigment, self-dispersing, unimodal, acrylamide, methacrylamide, vinyl acetate, sulfonic, sulfonate, anhydride, fluoromethacrylate